TITLE: PCB ANALYSIS BY GC-EC D

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Standard Operating Procedure for the Analyses of PCB's by GC-ECD EPA Method 8082A

1.0 Scope and Application:

1.1 This method is used to measure the PCB compounds in extracts prepared from aqueous matrices and/or solid matrices. The analyte list presented in this section identifies the possible group of compound amenable to this procedure; however, the analyte list presented in Appendix A is the group of analytes validated annually by the laboratory. This group of compounds is applicable to a variety of aqueous wastes matrices as well as aqueous sludge's, ground water, surface water, caustic liquors, acid liquors and water soluble solvents. The inclusion of additional analytes is limited only to performance evaluation of precision and accuracy studies using standards of known purity and successful completion of an MDL study.

1.2 It is applicable to TCLP extracts following any of the SW 846 extraction procedures.

1.3 It may also be applicable to Drinking water matrices but is not applicable for compliance purposes, the 500 series methods must be used instead.

1.4 This method may be used to determine the concentrations of various organochlorine PCB's in extracts from solid and liquid matrices, using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). The following PCB Arochlor compounds can be determined by this method using a dual-column analysis system; the individual polychlorodiphenyl compounds that make up an Arochlor mix are also included in the analyte list:

Compounds	CAS No. [a]	UPAC #
Aroclor 1016	12674-11-2	-
Aroclor 1221	11104-28-2	-
Aroclor 1232	11141-16-5	-
Aroclor 1242	53469-21-9	-
Aroclor 1248	12672-29-6	-

Aroclor 1254	11097-69-1	-
Aroclor 1260	11096-82-5	-
2-Chlorobiphenyl	2051-60-7	1
2,3-Dichlorobipheny	1 16605-91-7	5
2,2',5-Trichlorobiphenyl	37680-65-2	18
2,4',5-Trichlorobiphenyl	16606-02-3	31
Compounds	**CAS No.** [a]	**UPAC #**
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	44
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	66
2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	87
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	110
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	141
2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	151
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	187
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	206

[a] Chemical Abstract Service Registry Number

1.5 This method is exclusively for PCB's and the 19 individual polychlorobiphenyls (congeners) that make up a typical Arochlor mix.

1.6 This method includes a dual-column option that describes a hardware configuration in which two GC columns are connected to a single injection port and to two separate detectors. The option allows one injection to be used for dual-column simultaneous analysis. Under this configuration the amount of sample reaching the detector is reduced and therefore the MDL is also increased, a separate MDL study will be presented in Appendix A, specifying this configuration.

1.7 Extracts suitable for analysis by this method may also be analyzed for organochlorine pesticides (Method 8081) and organo-phosphorus pesticides (Method 8141).

1.8 The procedures may be appropriate for the analysis of these 19 congeners and may be used as a template for the development of a procedure for the determination of

other congeners not specifically included in this list. However, all 209 PCB congeners cannot be separated using the GC columns and procedures described in this method.

2.0 Minimum Detection Limit (MDL):

2.1 The detection limits presented in Appendix A were performed during the last 12 months, they are statistical values based on the procedure found in 40 CFR part 136 Appendix B and were calculated from actual analyses on BEL's GC/ECD instrument. The matrices were prepared in the laboratory with interference free reagents and materials. However, the practical quantitation limit (PQL) reported for each sample will depend on additional dilutions made if interferences or high values are encountered.

2.2 MDL determinations are performed annually on the most common matrices tested; however determinations on some of the least common matrices will be performed when the need is presented and samples become available.

3.0 Method Summary:

3.1 A measured volume of sample, approximately 1–L, is serially extracted with Methylene chloride at a neutral pH using a separatory funnel (method 3510),or a continuous (method 3520, continuous liquid-liquid) extractor. The Methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/ECD.

3.1.1 Method 3535 (solid-phase extraction), mat also be used but this technique requires that the sample be free of solids.

3.1.2 Solid samples may be extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3580A (Waste dilution for oils), Method 3541 (automated Soxhlet), method 3550 (ultrasonic extraction), or other appropriate technique or solvents.

3.2 Extracts for PCB analysis may be subjected to a sequential sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, this method is not applicable to the analysis of those compounds, if clean-up is used. Instead, use Method 8081.

3.3 The PCB compounds tested through this method are introduced into the GC/ECD system by direct injection of the dried concentrated solvent extraction. Qualitative

identification of the parameters in the extract is performed using the retention time at each of the columns; a positive match for a PCB will be the presence of a characteristic peak pattern at the expected RT of the major peaks in each column, GC/MS (e.g., Method 8270) is also recommended as a confirmation technique, if sensitivity permits.

3.4 The identification and quantification of the analytes is done through the software, however confirmation must be performed through visual inspection by the analyst. BEL assures adequate training, experience and supervision of the analyst, which is critical to acceptable performance in this test procedure.

3.5 The actual instrument conditions with gas flows, oven temperature ramp, injector and detector temperatures, valve timing, mass spectrophotometer voltages and the individual masses selected for detection, are all presented in Appendix B to this procedure.

4.0 Definitions:

The following definitions and acronyms are used in this method:

4.1 Initial Calibration Standards (ICS):
Standards prepared from pure analytes or commercially acquired in a mix for preparation of a calibration curve. A minimum of 5 standard concentrations levels are used to establish a linear working calibration range. The lowest of the group of standards should be at or below the necessary level to meet data quality objective of the project (or sample).

4.2 Initial Calibration Verification (ICV):
Standard prepared from pure analytes or commercially acquired in a mix for verification of the preparation of a calibration curve. It is of a different source or lot number (if from the same source) and analyzed at a mid-point of the calibration curve preferably with area counts within 50-200% of the internal standards (IS). This verification is performed once after establishing the calibration curve, prior to its use.

4.3 Calibration Verification Standard (CVS):
A standard prepared from the same source of the calibration standards at mid level of the working range, used to verify the validity of the calibration curve by meeting established verification criteria. This verification should be performed once every 12 hours and prior to sample analyses.

4.4 Internal Standards (IS):
1-Bromo-2-nitrobenzene is suggested for the analysis of the individual congeners. Prepare a solution of 5000 mg/L (5000 ng/µL) of 1-bromo-2-nitrobenzene. Spike 10 µL of this solution into each 1 mL of sample extract This standard introduced at the time of analyses that is used in the quantification formula for the analytes, the retention time should be similar to that of the target analytes being tested and prepared at the concentration specified. It is added to all samples, standards and blanks and the system is considered in control if the area counts from consecutive runs agree within 50-200%.

4.4.1 The area counts for an acceptable mid-level concentration for a CVS should have all the target compounds within 50-200% of the IS area counts.

4.5 Surrogate Standards (SS):
Standards introduced at the time of analyses that are used to monitor the systems performance during each run, it also monitors sample matrices and interference effects on the sample. Decachlorobiphenyl or tetrachloro-*m*-xylene have been found to be a useful pair of surrogates for both the single-column and dual-column configurations. The retention times should be similar to that of the target analytes being tested and are prepared to a concentration of 1.0 ug/L (concentration in the sample). They are added to all samples, standards and blanks and the sample is considered in control if their concentration recovery is within a QC established range.

4.7 Matrix Spike (MS):
A sample fortified with target compounds is an MS, the recoveries calculated after subtracting analytes present in the sample are used to evaluate accuracy of the test procedure in a particular matrix. Duplicate matrix spikes (MSD) performed on the same sample is used to evaluate precision statistics for that particular matrix.

4.8 Retention Time (RT):
Time of elution of a peak from the moment of injection to entrance and being detected by the Mass Spectrometer is called the absolute retention time (RT). The relative retention time is the elution time relative to another compound, in this case the IS peak established during the compound list compilation in the Chemstation software (see Appendix B).

4.9 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

5.0 Interferences and Contamination:

5.1 Interferences from Helium Gases, reagent water, reagents, standards, sorbent traps, non-PTFE lines tubing and rubber equipment material will be detected by the instrument. Phthalate esters are common contaminants that leach from plasticizers in rubber or plastic materials used in the sample preparation. They produce false positives that will be typically observed in the blank analyses run, subtraction of these false positive from the samples is not permitted. However the situation should cause the sample result to be flagged and a narrative explaining the finding presented in the report.

5.2 Sulfur (S8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur contamination should be expected with sediment samples. Sulfur can be removed through the use of Method 3660.

6.0 Safety:

6.1 The analyst should be aware that the Methylene Chloride used in the extraction by this method is a suspected carcinogen as is the majority of the compounds tested by this method, their standards should be handled with protective clothing in a well ventilated hood.

6.2 The instrument consumes Helium; this gas is typically supplied in cylinders. Proper gas cylinder handling techniques, gas lines connection and cylinder support are crucial to avoid accidents. An improperly supported cylinder that tips over and breaks the regulator or valve can become a dangerous gas propulsion object.

7.0 Equipment and Supplies:

7.1 **Agilent Model 6890 or 7683 automatic liquid sampler w/Dual Tower injectors** for simultaneous sample introduction, once the device injects the sample into each of the GC columns it sends the start signal to the GC, which will subsequently begin data acquisition and temperature programming.

7.3 **Agilent Injection port liners** (catalog No. 2-0478,25) designed for liquid sample introduction are best suited for use and if the column is a 0.53 mm ID it should be inserted 1 cm into the liner. Liners are the primary collection surface for contamination when injecting liquid directly into the system.

7.4 **Agilent Model 6890 and 6890N, Gas Chromatographic system** complete with a Chemstation data collection & data management software, temperature programmable oven, electronic pressure control, valve timing for gas flow movement, sample introduction interface and split-less injection port. It should also have the capacity to maintain constant flow through the column during desorption and temperature program cycle.

7.5 **Agilent Chemstation Data system** - A computer based system that allows the continuous acquisition and storage on machine-readable media of all the chromatographic data.

7.6 **GC Column Pairs**, the columns can be wide bore (53-mm) or narrow bore (0.25-mm) depending on the objective (more sample loading for lower detection 53-mm or better separation and resolution 25-mm or a compromise of both worlds 0.32-mm).

7.6.1 30-m x 0.32-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm film coating thickness or 1-µm film thickness.

7.6.2 30-m x 0.32-mm ID fused-silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), of same film thickness.

8.0 Reagents and Standards:

8.1 Commercially prepared standard mixes containing the target compounds typically tested are used by BEL in this method. The mix may contain more analytes than needed for the target list or it may be custom purchased containing only the targets. It is important to obtain the same standards list from two alternate sources or from the same source but two different lot numbers because verification checks are performed with second source standards. A second source is considered a separate vendor or a different lot number from the same vendor.

8.2 Surrogate Standards (SS) are purchased separately from the target compounds. No second sources are used here.

8.3 Methylene Chloride used for extraction and Hexane the extract transfer solvent also used to dilute commercial standards must be of the highest quality, always purchase a brand that states that it is suitable for extraction analyses containing the lowest residue after evaporation. Pesticide grade is a suitable grade.

8.4 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

9.0 Sample Collection, Preservation, Shipment and Storage:

9.1 Samples are collected in pre-cleaned new glass 1 liter bottles with Teflon lined covers. The sample is typically a composite sample and at least **two** 1 liter bottles are collected to have sufficient sample for quality control.

9.2 If the sample has residual chlorine it should be removed with ascorbic acid or the use of sodium thiosulfate.

9.3 The samples must be shipped in ice and/or stored in a cooler at below 4°C; the analyst has 7 days to perform the extraction. Once extracted the concentrate can be stored in a sealed vial for 40 days at <4 °C in the refrigerator prior to analyses.

10.0 Quality Control:

10.1 Quality Control procedures are necessary to evaluate the GC system operation as well as its stability throughout the run. The sample matrix amenability to the process is also tested with matrix spikes and matrix spike duplicates.

10.2 The GC/ECD system must be tested to determine that no residues in the system or inlet liner that may decompose the pesticides, this is done using an endrin/DDT mix to determine if endrin aldehyde, endrin ketone/DDE, DDD compounds are present (degradation by-products). Their presence at over 15% requires stopping for maintenance, usually the replacement of inlet liner is all that is needed. An example of the calculation is as follows:

$$\text{\% Breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD \% DDE)}}{\text{sum of all peak areas (DDT \% DDE \% DDD)}} \times 100$$

10.3 There must be an initial calibration of the GC/ECD system as described in following Section 11.0 of this procedure. In addition, the initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards). The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%.

10.2 The GC/ECD system must meet the 70-130% specification criteria for each CCV, each 12 hours and the pesticide degradation criteria daily.

10.3 Initial Demonstration of Proficiency (also known as Initial Demonstration of Capability) - Each analyst must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The analyst must also repeat this initial demonstration whenever significant changes in instrumentation are made. This is accomplished by analyzing 4 fortified samples, of the matrix under evaluation, and calculating the % recovery and the relative standard deviation between the four samples. They should produce similar recovery and precision data as produced by the laboratory in the past. The samples should be fortified with the target analytes at 10 to 50 times the established laboratory method detection limit (MDL).

10.3.1 If the samples are fortified at 10 times the laboratory desired MDL, the same data can then be used to establish the MDL, only 3 additional samples must be prepared and run to complete the 7 needed for an MDL study. The criteria established in 40 CFR parts 136; appendix B; still apply and must be meet for the data to be used to establish an MDL.

10.4 Before processing any samples, the analyst should also demonstrate, through the analyses of a method blank that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

10.5 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

10.6 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are

not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

10.7 Surrogate recoveries - The analyst must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory in previous analyses. Samples with surrogate recoveries under 10% must be re-injected; if the poor recovery persists the result must be reported with a flag noting the occurrence. The LCS recovery is very useful in these situations demonstrating that the system can perform acceptably in a clean matrix.

10.8 The experience of the analyst performing GC/ECD analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standards (ICV, CCV, etc.) should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are:

Do the peaks look normal?
Is the response obtained comparable to the response from previous calibrations?
Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc.
If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

11.0 Calibration and Standardization:

11.1 A standard containing a mixture of Arochlor 1016 and Arochlor 1260 will include many of the peaks represented in the other five Arochlor mixtures. As a result, a multi-point initial calibration employing a mixture of Arochlors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing multi-point initial calibrations for each of the seven Arochlors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Arochlors. This standard can also be used to determine the concentrations of either Arochlor 1016 or Arochlor 1260, should they be present in a sample.

11.2 Prepare a minimum of five calibration standards containing equal concentrations of both Arochlor 1016 and Arochlor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

11.3 Single standards of each of the other five Arochlors are required to aid the analyst in pattern recognition. Assuming that the Arochlor 1016/1260 standards described in Sec. 11.4 have been used to demonstrate the linearity of the detector, then these single standards of the remaining five Arochlors also may be used to determine the calibration factor for each Arochlor when a linear calibration model through the **origin** is chosen (see sec. 11.4). Prepare a standard for each of the other Arochlors. The concentrations should generally correspond to the **mid-point** of the linear range of the detector, but lower concentrations may be employed at the discretion of the analyst based on project requirements.

11.4 When PCBs are to be determined as Arochlors, an internal standard is typically not used, and decachlorobiphenyl is employed as a surrogate.

11.5 Proceed with the analysis of the calibration standards, inject 1-2 uL. Tabulate the area response of the minimum 5 characteristic RT against the concentration for each target Arochlor.

11.6 Using the external calibration technique, a min 0.99 correlation coefficient is required with a minimum of 5 standards.

11.7 Following the calibration curve preparation and analyses, the Chemstation software will calculate the correlation coefficient for each target compound.
Upon request the software will produce a curve for each target analyte. This information is written into the developed method and is evaluated upon request to the software (see entire printed method in appendix B) In addition, establishing the linear working range of the detector a criteria for establishing and demonstrating the desired sensitivity.

11.8 GC/ECD calibration verification; the verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

11.8.1 The initial calibration curve for each compound of interest should be verified prior to sample analysis, using a mid-point standard. The result should agree within 30% of the expected concentration. From their on, the calibration curve must be verified once every 12 hrs.

11.8.2 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/ECD system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze

a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

11.9 At the start of each day or at most every 24 hours, a degradation standard must be injected to verify system cleanliness. If degradation is excessive (>15%) and/or poor chromatography is visually noted, the injection port may require cleaning. It may also be necessary to break off the first 6 to12 in. of the capillary column. The use of a guard column between the injection port and the analytical column will help prolong analytical column performance life. The breaking off of column lengths may require adjustments of RT and/pr recalibration, both columns should be treated the same to reduce ID confusions.

11.10 DDT analog standard -- Used to determine if the commonly found DDT analogs (DDT, DDE, and DDD) elute at the same retention times as any of the target analytes (congeners or Arochlors), this made to avoid false positives. A single standard containing all three compounds should be sufficient. The concentration of the standard is mid-point calibration range of the Arochlor mix. When analyzing Pesticides under the same conditions as PCB's, this standard may me omitted if the individual DDT analogs RT's are already known.

12.0 Procedure:

12.1 The extraction of the sample must follow one of the extraction methods (3510C for aqueous samples, 3540C, 3550C for solid/soil samples or 3560 for oils). All sample extracts and standard solutions must be allowed to warm to ambient temperature before analysis. Add surrogates at time of sample extraction.

12.2 For aqueous samples, they are usually extracted using separatory funnel techniques. If emulsions cannot be broken with a glass rod or by adding Sodium Chloride (like Morton Salt) and it is clear that this will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction may be used. The separatory funnel extraction scheme described herein assumes a sample volume of 1 L.

12.3 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2–L separatory funnel. Pipette 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to neutrality (pH6.5 to 8) with Sodium Hydroxide solution or Hydrochloric Acid solution.

12.4 Add 60 mL of Methylene chloride to the sample bottle add 1 ppm of surrogates(Decachlorobiphenyl), seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min. with periodic venting to release excess pressure.
Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation.
The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the Methylene chloride extract in a 250 mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the Methylene chloride, corrected for the water solubility of Methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed to extract as described in method 3520C.

12.5 Add a second 60-mL volume of Methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

12.7 Pour the contents in a 1 mL Turbo-Vap evaporation flask. Bring the volume down 5 mL of volume and change solvent with 50 mL of Hexane. Bring the volume down below 1 mL without letting the solvent dry in the flask.

12.8 Quantitatively transfer the contents to a 1 mL volumetric flask and bring to volume with the Hexane solvent, cap and mix.

12.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL. Note this volume for final calculations.

12.10 Just prior to sample analyses add 10 uL of the Internal Standards (if using internal standards) to all samples, standards and blanks, mix (if using this technique). Transfer the contents and split into two auto sampler vials with glass inserts.

12.11 If the response for any pesticide exceeds the initial calibration range of the GC/ECD system, the sample extract must be diluted and reanalyzed. Additional internal standard solution must be added to the diluted extract to maintain the same concentration as in the calibration standards.

12.12 If the initial analysis of the sample or a dilution of the sample has a concentration

of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution.

12.13 When PCB's from the sample saturate the detector, this analysis must be followed by the analysis of organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

13.0 Calculation:

13.1 The concentration calculations are performed by the Chemstation software, if a dilution was made and the appropriate multiplication factor applied in the software, no further calculations need be done. If the dilution was performed and not entered into the data system then a manual calculation is required. If other than 1 liter of sample was extracted then apply the following equation:

Conc. Ug/L = 1000/ sample volume (mls)

13.2 Some Arochlor patterns will overlap on one column but separate clearly on the confirmation column, while others that separate clearly on the primary column will overlap on the confirmation column. The analyst will have to determine non-over-lapping PCB's of each column separately, meaning that not all the PCB's may be determined in one column.

13.3 Qualitative identification is performed by observing the peak RT vs. RT of the standard in each column.

14.0 Method Performance:

14.1 Method performance is annually calculated from the QA/QC data reported for the samples.

14.2 As a quality control check of method performance, the laboratory spikes all samples with the surrogate standard spiking solutions as described in Section 12.2, and calculates the percent recovery (R) of each surrogate compound. As part of the QC program for the laboratory, method accuracy for wastewater samples are assessed and records are maintained. From the analysis of spiked wastewater samples as detailed in Section 10.6, calculate the average percent recovery and the standard deviation of the percent recovery (s_R). Express the accuracy assessment as a percent recovery interval

from percent recovery $-2s_R$ to percent recovery $+2\ s_R$. For example, if percent recovery **$=90\%$ and $s_R = 10\%$, the accuracy interval is expressed as 70-110%. Update of the** accuracy assessment for each parameter is performed on an annual basis.

14.3 Method performance is also evaluated through Performance Evaluation (PE) Studies submitted to the laboratory by third party providers approved by EPA.

15.0 Pollution Prevention and Waste Management:

15.1 The laboratory pollution prevention and waste management program teaches the analyst where to dispose of his/her waste by department. This waste is segregated in labeled satellite areas throughout the laboratory prior to movement to the storage area for removal by a transporting and disposal entity in Lab-PACs.

15.2 Manifest are prepared and kept on file for inspection.

16.0 Data Assessment and Acceptance Criteria for Quality Control Measures:

16.1 The laboratory QA/QC department assesses data produced by each department following supervisor approval.
16.2 Acceptance criteria are established for all methods through data produced in the method. When insufficient data is available the method acceptance or performance criteria is used, in all cases the more stringent of the two are implemented.

17.0 Corrective Action for Out-of-Control Data:

17.1 BEL's QA/QC system is designed to monitor and detect Out-of-Control data as soon as it occurs. When the occurrence is detected the system is placed out of service until the appropriate corrective action can be administered.

17.2 Instruments are serviced by manufacturer trained professionals; BEL also has in-house professionals experienced in preventive maintenance techniques to diagnose problems that will enhance the preparation of a service technician prior to his arrival.

18.0 Contingencies for Out-of-Control Data or Unacceptable Data:

18.1 Out-of-Control data is retested if sufficient sample is available and/or the holding time has not expired. Otherwise data produced under these situations is flagged and a narrative is submitted with the report.

19.0 References:

19.1 SW846 Method 8000B

19.2 SW 846 Method 8082A

19.3 SW 846 Method 8000 update letter of December 17, 2007

19.4 Annual QA/QC Report for this Method.

APPENDIX A
Analyte list with Laboratory Method Detection Limit

Beckton Environmental Laboratories
Method Detection Limit 2010-2011

Area:GC
Analysis:TTO/PPO PESTICIDES
Method:608
Analist: Wanda Vázquez Bauzá
Instrument: GC ECD 6890

Contaminant	MDL ppm
Arochlor 1016	0.00034
Arochlor 1260	0.00038

APPENDIX B
Entire Method Printout from HP Chemstation Software

Method Information

PESTICIDES ANALYSIS
METHOD 8151

Method Change History

Operator	Date	Change Information
KHB	12/2/2008 3:56:47 PM	
KHB	6/22/2009 11:00:06 AM	added more autosampler washes
KHB	10/19/2009 4:46:06 PM	
KHB/WVB	10/20/2009 5:02:14 PM	
KHB/WVB	10/21/2009 11:39:18 AM	
KHB/WVB	10/21/2009 12:02:30 PM	
KHB/WVB	10/21/2009 12:02:56 PM	
KHB/WVB	10/21/2009 12:05:22 PM	
KHB/WVB	10/21/2009 12:08:15 PM	
KHB/WVB	10/23/2009 12:10:03 PM	
KHB/WVB	10/23/2009 12:11:11 PM	
WVB	11/17/2009 12:31:28 PM	
WVB	11/23/2009 12:23:17 PM	
WVB/KHB	2/18/2010 9:07:09 AM	
WVB/KHB	3/2/2010 3:05:41 PM	
WVB/KHB	3/2/2010 5:00:52 PM	
WVB	6/15/2010 2:30:50 PM	
WVB	6/28/2010 8:59:13 AM	

Run Time Checklist

Pre-Run Cmd/Macro:	off
Data Acquisition:	on
Standard Data Analysis:	on
Customized Data Analysis:	off
Save GLP Data:	off
Post-Run Cmd/Macro:	off
Save Method with Data:	off

Injection Source and Location

Injection Source: GC Injector

Injection Location: Front

6890 GC METHOD

OVEN
- Initial temp: 90 'C (On)
- Initial time: 3.00 min
- Ramps:

#	Rate	Final temp	Final time
1	5.00	200	6.00
2	10.00	260	7.00
3	0.0(Off)		

- Post temp: 50 'C
- Post time: 0.00 min
- Run time: 44.00 min
- Maximum temp: 320 'C
- Equilibration time: 0.00 min

FRONT INLET (SPLIT/SPLITLESS)
- Mode: Splitless
- Initial temp: 200 'C (On)
- Pressure: 9.32 psi (On)
- Purge flow: 50.0 mL/min
- Purge time: 0.60 min
- Total flow: 64.6 mL/min
- Gas saver: On
- Saver flow: 20.0 mL/min
- Saver time: 2.00 min
- Gas type: Helium

BACK INLET (SPLIT/SPLITLESS)
- Mode: Splitless
- Initial temp: 200 'C (Off)
- Pressure: 14.97 psi (Off)
- Purge flow: 50.0 mL/min
- Purge time: 0.75 min
- Total flow: 75.3 mL/min
- Gas saver: Off
- Gas type: Helium

COLUMN 1
- Capillary Column
- Model Number: Agilent DB-608
- Capilary Column Pest.
- Max temperature: 260 'C
- Nominal length: 30.0 m
- Nominal diameter: 530.00 um
- Nominal film thickness: 0.50 um
- Mode: constant flow
- Initial flow: 12.0 mL/min
- Nominal init pressure: 9.32 psi
- Average velocity: 83 cm/sec
- Inlet: Front Inlet
- Outlet: Front Detector
- Outlet pressure: ambient

COLUMN 2
- Capillary Column
- Model Number: Agilent DB-608
- Capilary Column Pest.
- Max temperature: 260 'C
- Nominal length: 30.0 m
- Nominal diameter: 530.00 um
- Nominal film thickness: 0.50 um
- Mode: constant flow
- Initial flow: 22.1 mL/min
- Nominal init pressure: 14.97 psi
- Average velocity: 130 cm/sec
- Inlet: Back Inlet
- Outlet: Back Detector
- Outlet pressure: ambient

FRONT DETECTOR (ECD)
- Temperature: 300 'C (On)
- Anode purge flow: 6.0 mL/min (On)
- Mode: Constant makeup flow
- Makeup flow: 60.0 mL/min (On)
- Makeup Gas Type: Argon methane 5%
- Adjust offset: 55.00
- Electrometer: On

BACK DETECTOR (ECD)
- Temperature: 300 'C (Off)
- Anode purge flow: 6.0 mL/min (Off)
- Mode: Constant makeup flow
- Makeup flow: 60.0 mL/min (On)
- Makeup Gas Type: Argon methane 5%
- Adjust offset: 56.00
- Electrometer: On

SIGNAL 1
- Data rate: 50 Hz
- Type: front detector
- Save Data: On
- Zero: 0.0 (Off)
- Range: 0
- Fast Peaks: Off

SIGNAL 2
- Data rate: 50 Hz
- Type: back detector
- Save Data: On
- Zero: 0.0 (Off)
- Range: 0
- Fast Peaks: Off

Attenuation: 0

COLUMN COMP 1
Derive from front detector

Attenuation: 0

COLUMN COMP 2
Derive from back detector

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

GC Injector

Front Injector:

Sample Washes	2	
Sample Pumps	3	
Injection Volume	1.0	microliters
Syringe Size	10.0	microliters
Nanoliter Adapter	Off	
PostInj Solvent A Washes	1	
PostInj Solvent B Washes	1	
Viscosity Delay	1	seconds
Plunger Speed	Fast	
PreInjection Dwell	0.00	minutes
PostInjection Dwell	0.00	minutes

Back Injector:
No parameters specified

Integration Events

Results will be produced with the enhanced integrator.

Default Integration Event Table "Event"

Event	Value	Time
Initial Slope Sensitivity	1.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.700	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_TCD"

Event	Value	Time
Initial Slope Sensitivity	100.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.000	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_ADC"

Event	Value	Time
Initial Slope Sensitivity	20.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.000	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_FID"

Event	Value	Time
Initial Slope Sensitivity	50.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.000	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_NPD"

Event	Value	Time
Initial Slope Sensitivity	500.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.000	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_FPD"

Event	Value	Time
Initial Slope Sensitivity	50.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.000	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_uECD"

Event	Value	Time
Initial Slope Sensitivity	500.000	Initial
Initial Peak Width	0.080	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.000	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_ECD"

Event	Value	Time
Initial Slope Sensitivity	50.000	Initial
Initial Peak Width	0.050	Initial
Initial Area Reject	5.000	Initial
Initial Height Reject	5.000	Initial
Initial Shoulders	OFF	Initial
Baseline at Valleys	ON	4.200
Fixed Peak Width	0.001	19.000

Apply Manual Integration Events: Yes

Advanced Baseline : No

Calibration Table

PESTICIDES ANALYSIS

Calib. Data Modified : 1/22/2004 3:48:25 PM

Calculate : External Standard
Based on : Peak Area

Rel. Reference Window : 5.000 %
Abs. Reference Window : 0.000 min
Rel. Non-ref. Window : 5.000 %
Abs. Non-ref. Window : 0.000 min
Uncalibrated Peaks : not reported
Partial Calibration : Yes, identified peaks are recalibrated
Correct All Ret. Times: Yes, even for non-identified peaks

Curve Type : Average Response/Amount
Origin : Ignored
Weight : Equal

Recalibration Settings:
Average Response : Average all calibrations
Average Retention Time: Floating Average New 75%

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Calibration Report Options :
Printout of recalibrations within a sequence:
Calibration Table after Recalibration
Normal Report after Recalibration
If the sequence is done with bracketing:
Results of first cycle (ending previous bracket)

Signal 1: ECD2 B,

RetTime [min]	Sig	Lvl	Amount [ng/ul]	Area	Amt/Area	Ref	Grp	Name
10.153	1	1	1.00000	1.97520e4	5.06278e-5	+I2		Tetrachloro-m-Xylene
		2	1.00000	2.14450e4	4.66308e-5			
		3	1.00000	2.04850e4	4.88161e-5			
		4	1.00000	1.85852e4	5.38063e-5			
		5	1.00000	1.89982e4	5.26366e-5			
		6	1.00000	1.79861e4	5.55986e-5			
11.405	1	4	1.50000	3.23013e4	4.64378e-5			Alpha-BHC
		5	2.50000	5.07801e4	4.92319e-5			
		6	3.50000	6.49272e4	5.39065e-5			
12.190	1	1	1.00000e-2	66.62350	1.50097e-4			Beta-BHC
		4	1.50000	1.23650e4	1.21310e-4			
		5	2.50000	2.10398e4	1.18822e-4			
		6	3.50000	2.77718e4	1.26027e-4			
12.400	1	4	1.50000	2.58954e4	5.79253e-5			Gamma-BHC (Lindane)
		5	2.50000	4.33244e4	5.77042e-5			
		6	3.50000	5.60079e4	6.24912e-5			
13.245	1	2	5.00000e-2	821.92261	6.08330e-5			Delta-BHC
		3	1.00000e-1	1484.33789	6.73701e-5			
		4	1.50000	2.90427e4	5.16480e-5			
		5	2.50000	4.60901e4	5.42416e-5			
		6	3.50000	5.94988e4	5.88247e-5			
14.791	1	2	5.00000e-2	526.05658	9.50468e-5			Heptachlor
		3	1.00000e-1	881.77441	1.13408e-4			
		4	1.50000	1.59823e4	9.38536e-5			
		6	3.50000	3.81259e4	9.18010e-5			
15.809	1	4	1.50000	2.50375e4	5.99102e-5			Aldrin
		5	2.50000	3.91221e4	6.39025e-5			
		6	3.50000	5.02066e4	6.97119e-5			
17.060	1	4	1.50000	2.28929e4	6.55225e-5			Heptachlor Epoxide
		5	2.50000	3.61959e4	6.90686e-5			
		6	3.50000	4.68788e4	7.46606e-5			
17.786	1	4	7.85849e-1	2.77517e4	2.83172e-5		1	Gamma-Chlordane
		5	1.31192	4.32680e4	3.03208e-5			
		6	1.83621	5.55193e4	3.30734e-5			
18.070	1	3	1.00000e-1	2043.89722	4.89261e-5			Alpha-Endosulfan
		4	1.50000	2.04834e4	7.32302e-5			
		5	2.50000	3.24459e4	7.70514e-5			
		6	3.50000	4.21119e4	8.31119e-5			
18.246	1	4	7.14151e-1	2.52197e4	2.83172e-5		1	Alpha-Chlordane
		5	1.18808	3.91837e4	3.03208e-5			
		6	1.66379	5.03060e4	3.30734e-5			
18.880	1	4	1.50000	2.12248e4	7.06719e-5			DDE
		5	2.50000	3.37575e4	7.40577e-5			
		6	3.50000	4.38632e4	7.97935e-5			
19.175	1	4	1.50000	2.54062e4	5.90407e-5			Dieldrin
		5	2.50000	3.94680e4	6.33425e-5			
		6	3.50000	5.06500e4	6.91017e-5			
19.491	1	2	5.00000e-2	42.42395	1.17858e-3			Endrin
		5	2.50000	2649.31274	9.43641e-4			
		6	3.50000	3794.75513	9.22326e-4			
19.770	1	4	1.50000	1.99943e4	7.50213e-5			Beta-Endosulfan
		5	2.50000	3.18680e4	7.84486e-5			
		6	3.50000	4.16266e4	8.40808e-5			
20.250	1	4	1.50000	1.42776e4	1.05060e-4			DDD
		5	2.50000	2.54026e4	9.84150e-5			
		6	3.50000	3.50577e4	9.98355e-5			

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RetTime [min]	Sig	Lvl	Amount [ng/ul]	Area	Amt/Area	Ref	Grp	Name
20.300	1	4	1.50000	2.28225e4	6.57245e-5			Endrin Aldehyde
		5	2.50000	3.43177e4	7.28486e-5			
		6	3.50000	4.34814e4	8.04942e-5			
21.043	1	2	5.00000e-2	1553.05823	3.21945e-5			DDT
		5	2.50000	3.09290e4	8.08302e-5			
21.396	1	4	1.50000	1.77616e4	8.44519e-5			Endosulfan Sulfate
		5	2.50000	2.95557e4	8.45861e-5			
		6	3.50000	3.90752e4	8.95708e-5			
23.089	1	5	2.50000	6029.85010	4.14604e-4			Methoxychlor
		6	3.50000	8727.84180	4.01016e-4			
27.730	1	1	1.00000	1.86005e4	5.37620e-5			Decachlorobiphenyl
		2	1.00000	2.01339e4	4.96674e-5			
		3	1.00000	4.44200e4	2.25124e-5			
		4	1.00000	1.94773e4	5.13418e-5			
		5	1.00000	2.00484e4	4.98793e-5			
		6	1.00000	1.93518e4	5.16748e-5			

More compound-specific settings:

Compound: Alpha-BHC
  Time Window : From 11.309 min To 11.553 min

Compound: Beta-BHC
  Time Window : From 12.124 min To 12.724 min

Compound: Gamma-BHC (Lindane)
  Time Window : From 12.362 min To 12.532 min

Compound: Delta-BHC
  Time Window : From 13.235 min To 13.435 min

Compound: Gamma-Chlordane
  Time Window : From 17.564 min To 17.992 min

Compound: Alpha-Endosulfan
  Time Window : From 17.887 min To 18.112 min

Compound: Alpha-Chlordane
  Time Window : From 18.211 min To 18.483 min

Compound: DDE
  Time Window : From 18.695 min To 19.045 min

Compound: Dieldrin
  Time Window : From 19.041 min To 19.231 min

Compound: Endrin
  Time Window : From 19.338 min To 19.678 min

Compound: Beta-Endosulfan
  Time Window : From 19.572 min To 19.932 min

Compound: DDD
  Time Window : From 20.195 min To 20.415 min

Compound: Endrin Aldehyde
  Time Window : From 20.146 min To 20.541 min

Compound: DDT
  Time Window : From 20.891 min To 21.151 min

Compound: Endosulfan Sulfate
  Time Window : From 21.276 min To 21.606 min

Compound: Methoxychlor

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Time Window : From 23.034 min To 23.184 min

Group summary :

Group 1 (Chlordane Mix) :
Group members:
Gamma-Chlordane with retention time 17.786 min
Alpha-Chlordane with retention time 18.246 min
Group Amount Calculation:
Level 4 with amount 1.50000 ng/ul
Level 5 with amount 2.50000 ng/ul
Level 6 with amount 3.50000 ng/ul

5 Warnings or Errors :

Warning : Overlapping peak time windows at 12.19 min, signal 1
Warning : Overlapping peak time windows at 17.786 min, signal 1
Warning : Overlapping peak time windows at 18.88 min, signal 1
Warning : Overlapping peak time windows at 19.491 min, signal 1
Warning : Overlapping peak time windows at 20.25 min, signal 1

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Peak Sum Table

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No Entries in table

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BECKTON ENVIRONMENTAL LABORATORIES, INC.

HISTORY OF REVISIONS

SOP NUMBER: _____

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE	APPROVED BY: